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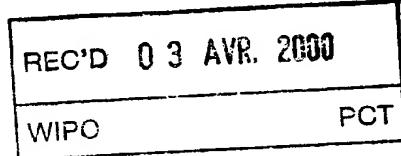
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I, LEANNE MYNOTT, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. PP 9360 for a patent by ENVIRONMENTAL SOLUTIONS INTERNATIONAL LTD filed on 22 March 1999.



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TEAM LEADER EXAMINATION
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ORIGINAL

AUSTRALIA

Patents Act 1990

PROVISIONAL SPECIFICATION

Invention Title: "Process and Apparatus for the Conversion of Carbonaceous Materials"

The invention is described in the following statement:

"Process and Apparatus for the Conversion of Carbonaceous Materials"

Field of the Invention

The present invention relates to a process and apparatus for the conversion of carbonaceous materials. More particularly, the process and apparatus of the present invention provides an improvement to the oil product of the conversion of the organic components of sewage and industrial sludges.

Discussion of the Prior Art

Sewage sludge is an unavoidable by-product of the treatment of sewage and other wastewaters. Traditionally, disposal of such sludge is expensive and typically constitutes half of the total annual costs of wastewater treatment. Historically, the major sludge disposal options have included agricultural utilisation, landfilling and incineration. Also historically, wastewater treatment plants have been designed to minimise sludge production and most effort is expended to stabilise and reduce the sludge volume prior to disposal or utilisation.

The solids component of sewage sludge comprises a mixture of organic materials composed of mostly crude proteins, lipids and carbohydrates. These solids further comprise inorganic materials such as silt, grit, clay and lower levels of heavy metals. For example, a typical raw sewage sludge comprises approximately 50 to 90% volatile matter and 25 to 40% organic carbon. Some sewage sludges already exceed current land application contaminant standards and consequently cannot be used agriculturally or are classified hazardous waste, largely due to their organochlorine content.

Many sludge processing options have been proposed in the past. Such options have the potential to convert a fraction of the organic material into usable energy and even less have been demonstrated as viable net energy producers at full

scale. One common process involves anaerobic digestion of sewage sludge in which approximately 25% of available organic materials is converted to produce a gas rich in methane. Historically, other alternatives have included starved air incineration and gasification.

A significant problem associated with the above processes relates to the fact that the principle usable energy-containing products are gases which are generally not easily condensable and are of a low net energy content. Accordingly, such gases are impossible or uneconomic to store and must generally be used immediately. Further, it is generally only practicable to use them to produce relatively low grade energy, such as steam, and flare them to waste during periods of little or no demand. Not surprisingly, it is preferable that any process used result in storable (liquid or solid), transportable and if possible, upgradable energy-containing products. Such products would include synthetic oils. It is consequently desirable that there be optimum production of storagable energy having any non-storable products, used in the operation of the process itself.

Disposal of sewage sludge has become more problematic recently due to the fact that;

- a) agricultural use of sewage sludge is restricted by its contaminant content, particularly the organochlorine content, and within this group the dioxins have become the limiting factor,
- b) ocean disposal is banned,
- c) landfilling is to shortly be banned in the European Union; and
- d) incineration of sewage sludge is opposed by the public primarily with respect to the dioxin issue (reformation of dioxin during hot flue gas cooling). Consequently recent research work on thermal sludge disposal processes concentrates on control of organochlorine compounds across the process.

In US Patents 4618735 and 4781796, there is described a process and apparatus for the conversion of sludges by heating and chemical reaction in order to obtain useful storable products therefrom, including oils. The process comprises the steps of heating dried sludge in a heating zone in the absence of oxygen to a temperature of at least 250°C for the volatilization of oil producing organic material therein, resulting in heating zone gaseous products and sludge residue, removing the said gaseous product from the heating zone; thereafter contacting heated sludge residue in a reaction zone with the removed heating zone gaseous products in the absence of oxygen at a temperature of 280°C to 600°C for repeated intimate gas/solid contact at temperatures sufficient to cause gas/solid contact, oil producing reactions to occur within the heating zone, gaseous products catalysed by the heated sludge residue resulting in reaction zone gaseous products containing oil products; removing the reaction zone gaseous products from the reaction zone and separating at least the condensable oil products therefrom.

Also disclosed is an apparatus for the conversion of sludge, said apparatus comprising an enclosure establishing a heated heating zone having an inlet thereto for dried sewage sludge and separate outlets therefrom for heating zone gaseous products and residual heating zone solid products; conveyor means within the heating zone enclosure for conveying solid products from its inlet to its solid products outlet; and enclosure establishing a heated reaction zone having separate inlets thereto for gaseous and solid products and separate outlets therefrom for gaseous and solid products; conveyor means within the reaction zone enclosure for conveying solid products from its solid products inlet to its solid products outlet; a heating zone solid products outlet being connected to the reaction zone solid products inlet for the passage of solid products between them; and duct means connecting the heating zone gaseous products outlet to the reaction zone gaseous products inlet.

In US Patents 5847248 and 5865956 there is disclosed a process and apparatus based on the process and apparatus of US Patent 4618735 and 4781796, with the following improvements.

The gaseous products from the heating zone are transferred to either an indirect or direct condenser with oil/water separation. The resulting oil and/or non-condensable products are injected into a second reactor. Sludge residue or char from the first reactor is transferred to the second reactor by way of a transfer line. The transfer line is equipped with a valve system to ensure that no gaseous products by-pass the condensation system.

In the second reactor, provided with heating means, the heated sludge residue from the first reactor is contacted with the revapourised oil or oil and non-condensable gaseous products from the condensation system in the absence of oxygen at a maximum temperature of 550°C. Such allows reductive, heterogenic, catalytic gas/solid phase reactions for the generation of clean products and high quality oil product. A conveyor and motor is provided to move the solid product or char through the second reactor.

Gaseous products are subsequently removed from the second reactor for passage through a further condenser and oil/water separation system or for ducting to a burner for direct combustion. In the case of passage through a further condenser and oil/water separation system a volume of non-condensable gaseous product, a volume of reaction water and a volume of refined, low viscosity oil is produced. Solid products or char are removed from the second reactor by way of a further transfer line having provided therein a screw conveyor for ensuring both no air ingress into and no gaseous product egress from the second reactor. The screw conveyor is connected to a cooling system to cool the solid product or char to less than 100°C before discharge to atmosphere.

The process and apparatus for the conversion of carbonaceous materials of the present invention has as one object thereof to provide a new process and

apparatus so as to obtain storage products with substantially unrestricted use therefrom.

It is a further object of the process and apparatus of the present invention to destroy at least in part ubiquitous, anthropogenic organochlorine pollutants, including AOX's, DDT, PCT's and PCDD/F's.

It is still a further object of the present invention to provide a method for the testing and control of the process of the present invention to provide optimum oil quality and organochlorine destruction.

Brief Description of the Invention

In accordance with the present invention there is provided a process for the conversion of sewage sludges, the process is comprising of the steps of:

- (a) feeding dried sludge through a reactor;
- (b) heating dried sludge in the reactor in the absence of oxygen for the volatilization of oil producing organic materials therein, resulting in gaseous products and sludge residue;
- (c) transferring sludge residue from the reactor to a storage bin through a valve system for ensuring both no air ingress into and no gaseous product egress from the reactor;
- (d) transferring the gaseous products from the reactor to a catalytic converter;
- (e) contacting the gaseous products from the reactor or the reheated oil and/or non-condensable products, if any, with a catalyst in the catalytic converter in the absence of oxygen;
- (f) removing the gaseous products from the catalytic converter; and
- (g) condensing and oil/water separating the gaseous products of the catalytic converter.

Preferably, the feeding of the dried sludge through the reactor utilises a feed system that ensures both no air ingress into, and no escape of gaseous products

from, the reactor. The heating of the sludge in the reactor is preferably conducted at a temperature of at least 250°C.

The process of the present invention may further comprise method steps of:

- transferring the gaseous products from the reactor to a condensation system to condense the oil product from the gaseous products; and
- reheating water free oil and/or non-condensable products, if any, from the condensation system in an oil reheatere.

The condensation system of step (g) may preferably comprise a direct condenser. The condensation of gaseous products of step (d) preferably comprises an indirect condenser with condensation taking place at >100°C.

The direct transfer of gaseous products of step (b) from the reactor to either the catalytic converter or the combustion system may take place in heat traced lines.

Still preferably the contact with the catalyst of step (e) occurs at temperatures of up to 650°C. At such temperatures reductive, catalytic gas/solid phase reactions are promoted and substantially eliminate hetero-atoms such as nitrogen, oxygen, sulphur, halogens, and the like.

The catalyst of the present invention may preferably comprise materials such as activated alumina, γ -aluminium oxide, silicon oxide and oxides of alkali, earth alkali and transition metals such as copper, iron, magnesia, nickel, sodium and zinc and mixtures therefrom.

The process of the present invention may preferably still further comprise the step of testing the miscibility of the oil product with a hydrocarbon solvent such as diesel fuel. In response, the catalytic converter conditions may be modified, thereby optimizing the catalytic conversion of sewage sludge, particularly the elimination of hetero-atoms such as halogens, nitrogen, oxygen and sulphur.

The present invention still further provides a process for the optimisation of the process for the conversion of sewage sludges as set out above with particular relevance to the removal of hetero-atoms to produce a product miscible with a hydrocarbon solvent such as diesel fuel. Oils miscible in a hydrocarbon solvent have lower viscosity, water content and hetero-atom content, i.e. a higher oil quality. Consequently the miscibility with a hydrocarbon solvent can be used as an analytical tool to optimize the process.

In accordance with the present invention there is further provided an apparatus for the conversion of carbonaceous materials, the apparatus comprising a feed system for dried material to be conveyed, a reactor, and a catalytic converter, the reactor having a solid product discharge outlet and a transfer line provided for transport of gaseous product directly or indirectly to the catalytic converter.

In one form of the present invention a first condensation system is provided, in conjunction with a reheater, in-line between the reactor and catalytic converter. The first condensation system may include an oil/water separation system. The catalytic converter is further adapted to contact heated catalyst contained therein with oil or oil and non-condensable products of the condensation system, wherein gaseous products may be removed from the catalytic converter.

Preferably, a second condensation system is provided to receive gaseous product from the catalytic converter.

Description of the Drawings

The present invention will now be described, by way of example only, with reference to two embodiments thereof and the accompanying drawing, in which:

Figure 1 is a schematic diagram of an apparatus for the conversion of carbonaceous materials in accordance with a first embodiment of the present invention.

Description

In Figure 1 there is shown an apparatus 10 for the conversion of sludges. The apparatus comprises a feed system 12 for dried sludge 14. The feed system 12 feeding said sludge 14 to a reactor 16. The feed system 12 is such that it ensures both no air ingress and no gaseous egress from the reactor 16.

The reactor 16 is provided with heating means 18 thereabout, such that dried sludge may be heated therein in the absence of oxygen to at least 250°C. This results in the volatilization of oil producing organic materials in the reactor 16. Further, this reaction provides gaseous products and sludge residue or char. A screw conveyor 20 and a motor 22, or their equivalent, is provided to move the sludge through the reactor 16.

The gaseous products from the reactor 16 are either transferred to a combustion system 24, to a catalytic converter 26 or to a first condensation system 28 with oil/water separation. Further, the first condensation system 28 may comprise either a direct or an indirect condenser. The resulting oil is injected, via line 30, with or without any non-condensable products, via line 32, from the first condensation system 28 into an oil reheat 34 where the oil and/or non-condensable products 32 are heated in the absence of oxygen to a maximum temperature of 650°C.

The gaseous products from the reactor 16 or the preheated oil and/or non-condensable products from the oil reheat 34 are injected into the catalytic converter 26, via lines 31 and 33 respectively. The catalytic converter 26 is provided with a heating means 36 thereabout such that the preheated oil and/or non-condensable products may be heated therein in the absence of oxygen to a maximum temperature of 650°C. This allows reductive, catalytic removal of hetero-atoms to produce an oil product of a viscosity that is lower than that of diesel. The refined gaseous products from the catalytic converter 26 are

transferred, via line 37, to a final or second condensation system 38 with oil/water separation.

The solid product or char of the reactor 16 is removed from the reactor 16 by way of a transfer line 40. The transfer line 40 is equipped with a valve system 42 and a screw conveyer (not shown). The valve system 42 is such that it ensures both no air ingress and no gaseous egress from the reactor 16. The screw conveyer is connected to a cooling system 44 to cool the solid products or char to less than 100°C.

A second embodiment of the present invention comprises the apparatus for the conversion of sludges as described in US Patents 5847248 and 5865956, the content of which is incorporated herein by reference, with addition of the oil reheater 34 and catalytic converter 26 as described above for the apparatus 10.

The present invention may be further described with reference to the following example.

Example

The sewage sludge employed in the determination of process data using the continuous apparatus of the present invention was raw sludge from two locations, being the Subiaco Waste Water Treatment Plant (WWTP), Perth, Western Australia, and the Atlanta WWTP, Georgia, United States of America. The sludges were dried to approximately 95% dryness in a drying oven at 70°C prior to processing.

The sludges were processed in either the apparatus 10 described hereinabove or in an apparatus according to the second embodiment of the present invention, that apparatus characterised by utilising both a first and second reactor, char from the first reactor being transferred to the second reactor and the gaseous products of the first reactor being condensed prior to their injection to the second reactor.

The first series of tests were conducted to demonstrate the impact of the catalytic converter on oil quality. Results are shown in Table 1.

Table 1 - Oil Quality Data: Impact of Catalytic Conversion

Item	Run 1	Run 2	Run 3	Run 4	Run 5
Viscosity @ 40°C [cSt]	25.8	29.8	3.2	7.7	7.5
Water Content [%]	9.4	6.7	0.72	2.2	-

Run 1: Subiaco sludge was processed as per US patent 5847248. As such, gaseous products are condensed after the first reactor and the oil product is injected into the second reactor. Both reactors were operated at 450°C, with the feedrate being 600g/hr. No catalyst used.

Run 2: Conversion of raw sludge from the Atlanta WWTP, otherwise as per Run 1.

Run 3: Subiaco sludge processed in accordance with the present invention with gaseous products being condensed and the oil product, after passing through the reheater being contacted with the catalyst (aluminium oxide impregnated with transition metal oxides) in the catalytic converter. The catalytic converter temperature was maintained at 400°C.

Run 4: As per Run 3, with gaseous products being directly transferred to the catalytic converter.

Run 5: Atlanta sludge processed as per Run 3.

The above results clearly show that the oil viscosity and water content are reduced significantly by the use of the catalytic converter.

A second series of tests was conducted to determine the influence of catalyst support. Test results are shown in Table 2.

Table 2: Oil Quality versus Catalyst Support

Item	Run 6	Run 7	Run 8	Run 9	Run 10	Run 11
Viscosity @ 40 ⁰ C [cSt]	20.9	21.4	7.8	4.7	4.8	27.8
Water Content [%]	1.1	4.4	1.7	1.5	-	4.6

Run 6: Atlanta sludge was processed in accordance with the present invention with gaseous products being condensed and the oil product being preheated prior to injection into the second reactor from where it is transferred to the catalytic converter. The temperature of both reactors and catalytic converter was controlled at 450⁰C. Sludge feed rate was controlled at 600 g/hr. Pure Al₂O₃ was used as a catalyst and was activated at 600⁰C.

Run 7: As per Run 6, with Al₂O₃ being activated at 1200⁰C as a catalyst.

Run 8: As per Run 6, with Al₂O₃ being impregnated with transition metal oxides and catalytic converter temperature being 400⁰C.

Run 9: As per Run 6, using silica gel as catalyst.

Run 10: As per Run 6, processing Subiaco sludge and using zeolite as catalyst with catalytic converter temperature being 420⁰C.

Run 11: As per Run 6, using char as catalyst

The results show that pure Al_2O_3 is not as good as Al_2O_3 doped with transition metals. Silica gel appears to be a good catalyst and the conversion char is not as good as Al_2O_3 as a catalyst.

A third series of tests were conducted to assess the impact of catalyst temperature on oil quality and yield. Results are shown in Table 3.

Table 3: Oil Quality and Yield versus Catalyst Temperature

Item	Run 12	Run 13	Run 14	Run 15	Run 16	Run 17	Run 18	Run 19	Run 20
Viscosity @ 40°C [cst]	12.4	8.9	31.7	28.4	26.2	30.3	26.8	16.5	16.4
Oil Yield [%]	23.3	17.9	25.1	25.3	22.8	22.5	22	21.4	19.6

Run 12: Conversion of Subiaco sludge with gaseous products being condensed and the oil product being preheated prior to injection into the catalytic converter. The temperature of reactor and catalytic converter was controlled at 450 and 400°C respectively. Sludge feed rate was controlled at 600 g/hr. Zeolite was used as a catalyst.

Run 13: As per Run 12, with catalyst temperature being 420°C.

Run 14: As per Run 12, with gaseous products being directly transferred to the catalyst and a catalyst temperature of 450°C.

Run 15: As per Run 14, with catalyst temperature being 470°C.

Run 16: As per Run 14, with catalyst temperature being 500°C.

Run 17: As per Run 14, with catalyst temperature being 520°C.

Run 18: As per Run 14, with catalyst temperature being 530°C.

Run 19: As per Run 14, with catalyst temperature being 540°C.

Run 20: As per Run 14, with catalyst temperature being 550°C.

The above results indicate that the optimal temperature using a zeolite catalyst is 400 to 420°C, when using intermediate condensing and 530-550°C without intermediate condensing.

A fourth series of tests were conducted to asses the impact of catalyst to oil vapour ratio on oil quality. Results are shown in Table 4.

Table 4: Catalyst to oil vapour ratio versus oil Quality

Item	Run 21	Run 22	Run 23
Weight Hourly Space Velocity (WHSV) [hr ⁻¹]	2.3	1.1	0.7
Viscosity @ 40°C [cSt]	13	4.5	4.8
Water Content [%]	3.6	1.2	1.1
Oil Yield [%]	23.2	18.8	18.3

Run 21: Conversion of Atlanta sludge with gaseous products being condensed and the oil product being preheated prior to injection into the second reactor from where it is transferred to the catalytic converter. The temperature of both reactors and the catalytic converter were

controlled at 450°C. Sludge feed rate was controlled at 600 g/hr. Aluminium oxide impregnated with transition metal oxides was used as a catalyst and 80 g of catalyst used.

Run 22: As per Run 21, with 165 g of catalyst being used.

Run 23: As per Run 21, with 265 g of catalyst being used.

As expected, the results show improved oil quality at lower WHSV (higher catalyst mass), albeit at a reduced oil yield. There does not appear to be any further improvement in oil quality by reducing the WHSV to below 1 hr⁻¹.

A fifth series of tests was conducted to assess the impact of catalyst regeneration on oil quality. Results are shown in Table 5.

Table 5: Catalyst regeneration versus Oil Quality

Item	Run 24	Run 25	Run 26	Run 27	Run 28	Run 29
Viscosity @ 40°C [cSt]	11.8	17.0	14.6	17.5	20.5	20.2
Oil Yield [%]	16.8	20.6	19.7	16.8	17.1	19.2

Run 24: Subiaco sludge was processed with gaseous products being transferred directly to the catalytic converter. The temperature of the reactor and the catalytic converter was controlled at 450 and 550°C respectively. Sludge feed rate was controlled at 600 g/hr. 210 g of native zeolite was used as a catalyst.

Run 25: As per Run 24, with the catalyst being regenerated on-line for the first time.

Run 26: As per Run 24, with the catalyst being regenerated on-line for the second time.

Run 27: As per Run 24, with the catalyst being regenerated on-line for the third time.

Run 28: As per Run 24, with the catalyst being regenerated on-line for the fourth time.

Run 29: As per Run 24, with the catalyst being regenerated on-line for the fifth time.

The results show a slight deterioration in catalyst efficacy via on-line regeneration. However, performance appeared to stabilise after 3 or 4 regenerations.

A sixth series of tests were conducted to compare oil yield and quality from the dual reactor system with intermediate condensation and the single reactor system without intermediate condensation. The results are shown in Table 6.

Table 6: Oil Quality Data: Impact of Dual versus Single Reactor Systems

Item	Run 30	Run 31
Weight of Catalyst [g]	165	163
Oil Yield [%]	18.8	16.9
Viscosity [cSt]	4.5	7.6

Run 30 Atlanta WWTP sludge was processed with gaseous products being

condensed after the first reactor and the oil product was injected into the second reactor. The temperature of the reactor and the catalytic converter was controlled at 450°C. Sludge feed rate was controlled at 600 g/hr. Al₂O₃ was used as the catalyst.

Run 31: As per Run 30 but without the intermediate condensing of gaseous products or the second reactor.

These results indicate that the presence of the second reactor, and the condensation of gaseous products before injection thereto, does not have a significant impact upon oil yield and quality, as might otherwise have been expected, when compared with the apparatus 10 utilising the single reactor 16.

A seventh series of tests was conducted to determine the impact of intermediate condensation on oil yield and quality in the single reactor system. Test results are shown in Table 7.

Table 7: Oil Quality Data: Impact of Intermediate Condensation

Item	Run 32	Run 33
Weight of Catalyst [g]	180	210
Catalyst Temperature [°C]	420	550
Oil Yield [%]	23.3	15.7
Viscosity [cSt]	8.9	11.8

Run 32 Subiaco sludge was processed with gaseous products being condensed after the single reactor prior to injection to the catalytic

converter. The temperature of the reactor and the catalytic converter was controlled at 450°C. Sludge feed rate was controlled at 600 g/hr. Zeolite was used as the catalyst.

Run 33: As per Run 32 but without the condensing of gaseous products prior to introduction to the catalytic converter.

These results indicate that the condensing of the gaseous products of the single reactor prior to injection to the catalytic converter provides an improved oil quality and yield when compared with not having conducted the condensation step, when using zeolite as the catalyst.

The process for the conversion of sewage sludges of the present invention may be optimised with regard to removal of hetero-atoms through use of miscibility with a standard hydrocarbon source such as diesel fuel. It is apparent that the miscibility with diesel fuel is significantly influenced by the presence of hetero-atoms such as oxygen, nitrogen and sulphur. Such hetero-atoms particularly oxygen and sulphur and to a lesser degree nitrogen are removed by the catalytic converter generating an oil that is miscible at any ratio with diesel fuel. Accordingly, the miscibility of the oil product is a direct measurement of the quality of the oil. The miscibility can be directly correlated with viscosity, meaning the better mixing the lower the viscosity. As stated in US Patent 5847248, viscosity can also be used as an indicator for the destruction rate of organochlorine compounds and consequently, since the heavy metal oxides present in the catalytic converter are the same as in sewage sludge, the dehalogenation of organochlorines will take place in the catalytic converter at a much higher rate than in the second reactor of US Patents 5847248 and 5865956, and miscibility can also be used as a control tool for organochlorine destruction.

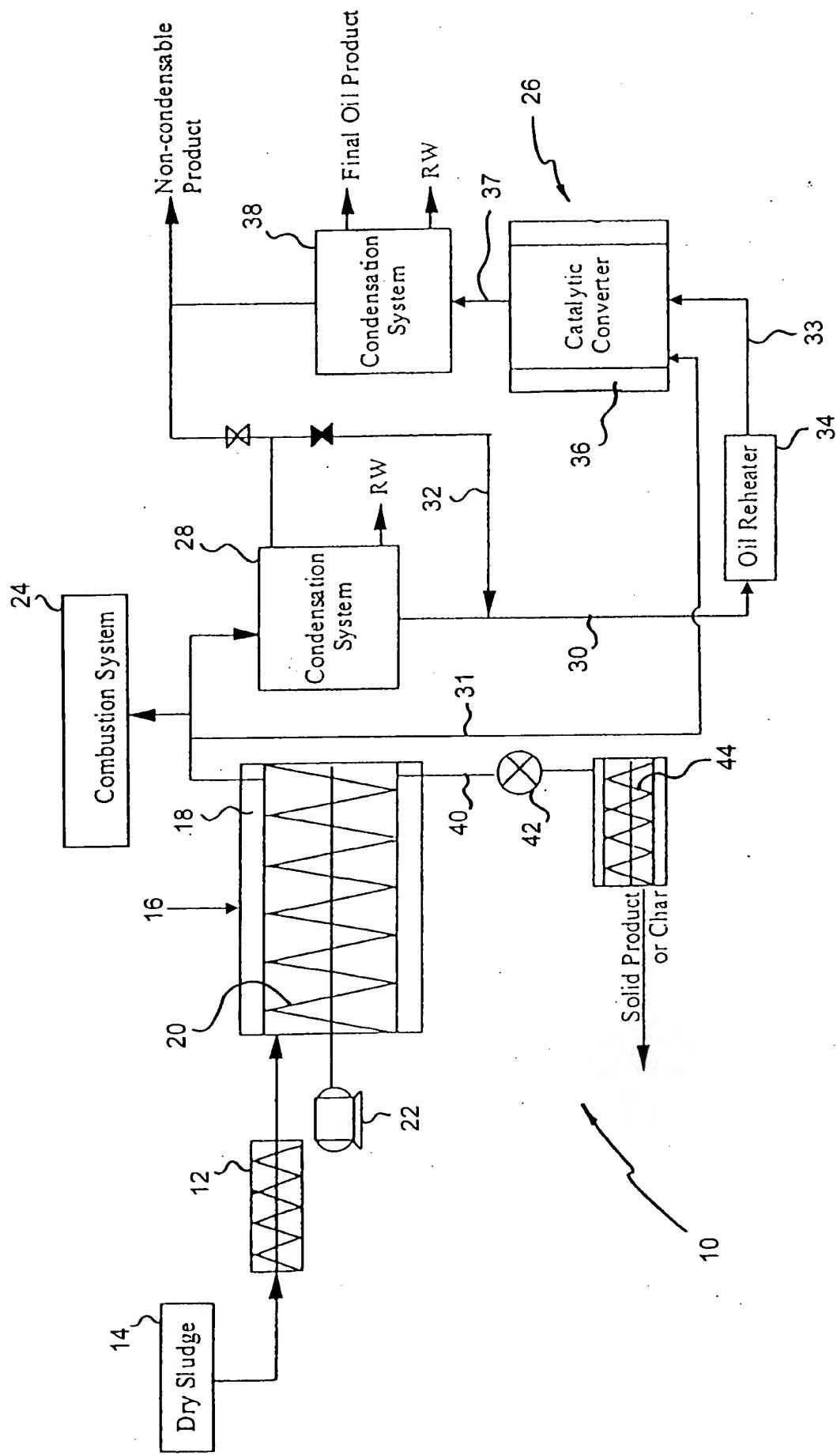
The process and apparatus of the present invention provide reductive, thermal heterogenic catalytic solid/gas phase reactions in order to obtain storable products with unrestricted use.

Modifications and variations such as would be apparent to the skilled addressee are considered to fall within the scope of the present invention.

Dated this twenty-second day of March 1999

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